Nanotechnology Advantages Applied to Gas Sensor Development

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ABSTRACT

Gas detection instruments are increasingly needed for industrial health and safety, environmental monitoring, and process control. To meet this demand, considerable research into new sensors is underway, including efforts to enhance the performance of traditional devices, such as resistive metal oxide sensors, through nanoengineering. Metal oxide sensors have been utilized for several decades for low-cost detection of combustible and toxic gases. However, issues with sensitivity, selectivity, and stability have limited their use, often in favor of more expensive approaches. Recent advances in nanomaterials provide the opportunity to dramatically increase the response of these materials, as their performance is directly related to exposed surface volume. The recent availability of various metal oxide materials in high-surface-area nanopowder form, as well as implementation of newly developed nanofabrication techniques, offer tremendous opportunities for sensor manufacturers.

INTRODUCTION

Resistive metal oxide sensors comprise a significant part of the gas sensor component market, which generated revenues of approximately \$1.5B worldwide in 1998. Significant growth is projected, and the market should exceed \$2.5B by 2010. While many different approaches to gas detection are available (see **Figure 1**), metal oxide sensors remain a widely used choice for a range of gas species. These devices offer low cost and relative simplicity, advantages that should work in their favor as new applications emerge.

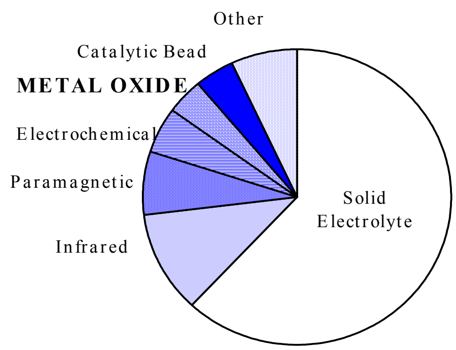

Figure 1. Gas sensor market divided by technology area.

Numerous materials have been reported to be usable as metal oxide sensors including both single- (e.g., ZnO, SnO_2, WO_3, TiO_2, and Fe_2O_3) and multi-component oxides ($BiFeO_3$, $MgAl_2O_4$, $SrTiO_3$, and $Sr_{1-y}Ca_yFeO_{3-x}$) [1]. The mechanism for gas detection in these materials is based, in large part, on reactions that occur at the sensor surface, resulting in a change in the concentration of adsorbed oxygen. Oxygen ions adsorb onto the material's surface, removing electrons from the bulk and creating a potential barrier that limits electron movement and conductivity. When reactive gases combine with this oxygen, the height of the barrier is reduced, increasing conductivity. This change in conductivity is directly related to the amount of a specific gas present in the environment, resulting in a quantitative determination of gas presence and concentration.

These gas-sensor reactions typically occur at elevated temperatures (150-600°C), requiring the sensors to be internally heated for maximum response. The operating temperature must be optimized for both the sensor material and the gas being detected. In addition, to maximize the opportunities for surface reactions, a high ratio of surface area to volume is needed. As an inverse relationship exists between surface area and particle size, nano-scale materials, which exhibit very high surface area, are highly desirable.

Several recent research reports have confirmed the benefits of "nanoengineering" on sensor performance. For example, Rella, et al. [2] demonstrated good response to NO_2 and CO when the SnO_2 grain size was controlled below 10 nm. Ferroni, et al. [3] demonstrated good response to NO_2 for solid solutions of TiO_2 and WO_3 when grain size was held at near 60 nm. Chung, et al. [4] demonstrated that increasing the firing temperature (which increases grain size) significantly reduces the response of WO_3 sensors to NO_x. Chiorino, et al. [5] also demonstrated that firing temperature plays a key role in the response of SnO_2 sensors, with films treated to 650°C showing nearly twice the response to NO_2 as films treated at 850°C.

THICK FILM GAS SENSORS

Nanomaterials Research has also been pursuing studies related to the use of nano-sized metal oxide materials for gas sensors since its founding in 1994. The company focuses primarily on new sensor materials, material combinations, and microstructure control. State-of-the-art metal oxide sensors are typically based on only one material, namely tin oxide (SnO_2). In contrast, Nanomaterials Research employs a wide range of nano-scale ceramics, coupled with specifically added polymers and metals. As the result of considerable in-house research, a significant body of knowledge now exists within the company regarding the effects of composition and microstructure on sensor performance.

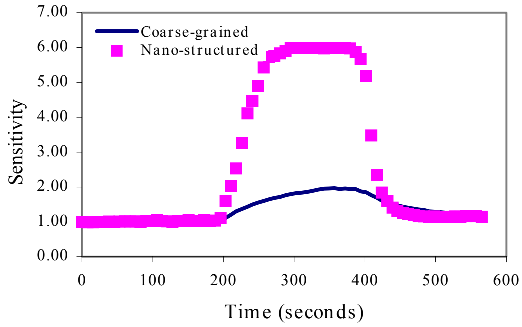

Figure 2. Comparison of sensors produced from micron- and nano-sized powders.

Results to date confirm the findings of other researchers with respect to the role of grain size on sensor response. For example, Figure 2 shows the effects of starting particle size on the company's NO_x sensor. Course-grained devices were produced from commercial powders (> 1 μm), while fine-grained devices were produced from specially prepared nanopowders (< 100 nm). In addition to the enhanced sensitivity demonstrated by the nanostructured sensors, the sensors responded more quickly, a distinct advantage for certain applications.

However, it should be noted that the effects of grain size are often complicated by other factors, in particular those related to heat treatment of the sensor during manufacturing. The majority of the sensors produced at Nanomaterials Research are fabricated by screen-printing, a traditional, low-cost, thick film deposition process. In this technique, multiple layers (including the sensor material itself) are deposited onto rigid substrates and heated to a relatively low temperature to partially densify the sensor film (see Figure 3). These substrates are then integrated into modified electronic packages, such as TO-style headers, for drop-in application in gas detection instruments. Nanomaterials Research has demonstrated the capability to produce, assemble, and test prototype sensors in this configuration and already sells prototype quantities of certain sensors (e.g., our trace-level H_2 sensor) for customer evaluation.

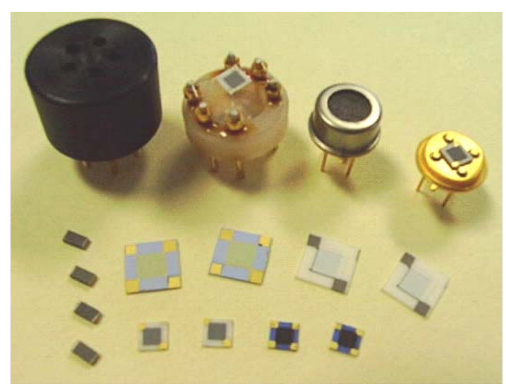

Figure 3. Various gas sensor prototypes fabricated by Nanomaterials Research.

Proper control of grain size remains a key challenge for high sensor performance. The thick film devices must be heated to sufficiently high temperatures to ensure interconnectivity between individual grains and film robustness. However, if the processing temperature is too high, substantial grain growth can occur, coupled with a rapid decrease in open porosity, resulting in a marked decrease in sensor response (see Figure 4). To further complicate matters, many metal oxides of interest to sensor research can assume multiple oxidation states, each of which can behave very differently when exposed to gas. These factors must be taken into account when one develops and demonstrates a new sensor device.

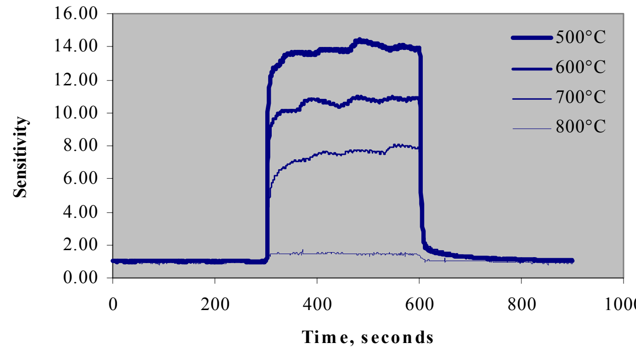

Figure 4. Effect of different processing temperatures on sensitivity for SnO_2.

MULTILAYER SENSOR ARCHITECTURES

In addition to optimizing the sensor material, Nanomaterials Research is also developing techniques to improve sensor manufacture. Thick film fabrication typically involves considerable manual labor, which unfortunately limits reproducibility from part to part and makes cost reduction difficult. Recently, however, Nanomaterials Research demonstrated and patented an alternative fabrication process for preparing metal oxide sensors (US # 6,202,471), which many overcome many of these disadvantages.

This new approach produces chip-style sensors with a layered design and a series of internal electrodes. Similar fabrication processes are currently used to produce surface-mount electronic components (e.g., capacitors) which range in cost from a few cents to a few dollars per part depending on complexity, footprint, and production volume. Such components are fabricated by casting thin ceramic sheets [6,7]. Electrodes are deposited on certain sheets, and the different layers are interleaved to form the desired configuration. Figure 5 shows a roll of WO_3 sensor tape and cross-sections from two different sensor devices produced at Nanomaterials.

Multilayer gas sensors offer several advantages compared to conventional thick-film devices. In particular, the sensors can be produced in larger batches using automated techniques, reducing labor costs and increasing reproducibility. However, more importantly, the process allows the manufacturer to tailor electrical properties of the sensor by altering certain design parameters. For example, devices can be fabricated with a specific resistance baseline resistance by controlling the number of internal layers (see Figure 5), layer thickness, and the area under the electrodes.

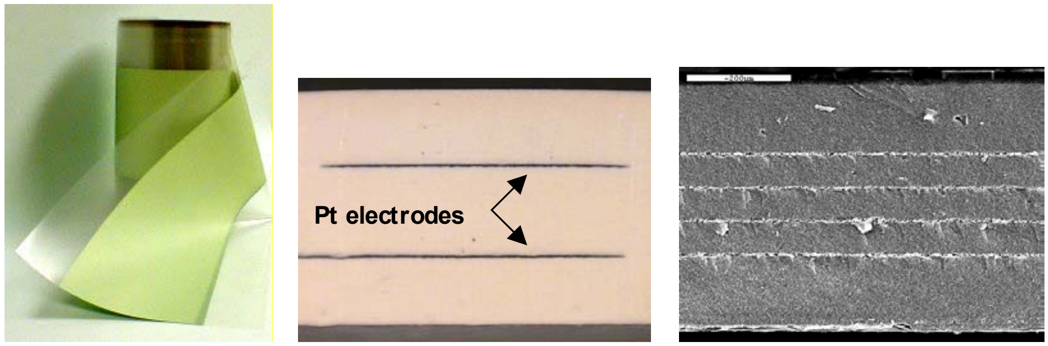

Figure 5: Ceramic tape with prototype multilayer sensor devices.

The advantages associated with resistance tailoring are particularly important for developing affordable electronics for processing sensor outputs. Many metal oxides exhibit very high resistances, requiring complicated circuitry to precisely measure in the MΩ range. Meanwhile, other materials have high conductivity, making it difficult to detect decreases in resistance after gas exposure. Typically, secondary materials must be added to alter resistance, often with an adverse effect on gas response, making a new method of tailoring resistance of great interest to sensor designers.

However, despite the many advantages associated with multilayer processing, issues do exist with respect to the sensor's microstructure and the ability to retain fine grains after thermal processing. Thick film sensors are supported on a rigid substrate, allowing the materials to be processed to a less dense state and reducing the chance for grain growth during heat treatment. Conversely, multilayer sensors must be self-supporting, requiring more complete densification. Higher processing temperatures are typically utilized, porosity is lower, and the final grain size is often much larger.

An example of the different microstructures that can result when multilayer sensors are heated to steadily increasing temperatures is shown in Figure 6. Raw materials in the 60-80 nm size range were used to prepare the sensors. At the lowest processing temperature, the components were less than 50% dense, and the grains were on the same order as the starting powder. However, by 1125°C, the devices had less than 3% porosity, and significant grain growth had occurred. Optimum performance was found at 1000°C (middle, top). At this condition, grain size remained small, porosity was high, and the sensors were sufficiently robust for handling and packaging.

NANOFABRICATED SENSOR DEVICES

In addition to its extensive research on the use of nanopowders in gas sensor devices, Nanomaterials Research is also tapping into the growing trend of micro- and nano-fabrication to improve its gas-sensing devices. The company's approach in this area is built around a unique self-organized and nanostructured platform material, namely anodic aluminum oxide (AAO). AAO is robust, chemically stable, refractory, and micromachinable, making it an ideal choice for metal oxide sensor design.

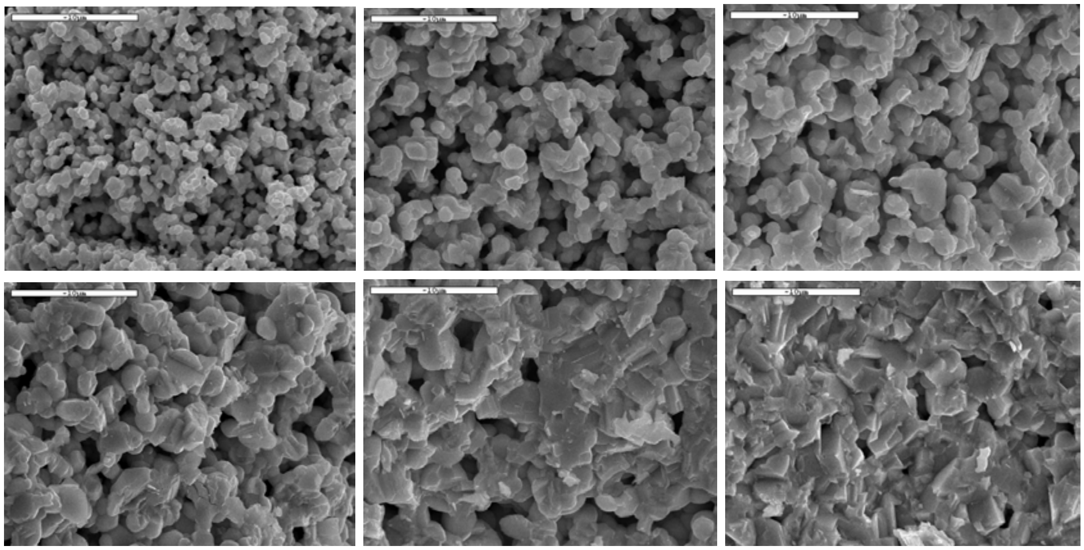

Figure 6. SEM images showing decreased porosity and increased average grain size as the soak temperature is increased from 975°C to 1125°C.

When aluminum is anodized in an acid solution, an oxide film is created that consists of uniform and parallel nano-sized pores (see Figure 7). The resulting pore diameter is tunable from a few nanometers to several hundred nanometers [8], and the dimensions and morphology of the pores can be engineered with high precision. The result is a tailorable "nanotemplate" into which a variety of metal oxide sensor materials can be deposited by either wet chemical or gas-phase processes. Moreover, its intrinsic morphology and chemistry permits micromachining of the AAO material, enabling the fabrication of a ceramic MEMS platform, in which very-high-surface-area sensor materials are intimately embedded.

Nanomaterials Research has already demonstrated a range of microsensor components based on this platform, including metal oxide sensors for detecting indoor air pollutants and miniature catalytic sensors designed for very low-power operation. In addition, the base material provides a mechanism for detecting humidity if the porosity is precisely controlled and appropriate surface coatings are applied.

SUMMARY

The recent advances in nanomaterials have created tremendous opportunities for improved gas sensor devices. Based on its research efforts over the past several years, Nanomaterials Research now offers prototype thick film devices for detecting both low-level (10-1000 ppm) and high-level (> 1%) concentrations of hydrogen. Sensors for detecting NH_3, NO_x, VOCs, and CO_2 are in development. In addition, the company is continuing to pursue alternative fabrication techniques such as multilayer processing and nanofabrication, which offer advantages in miniaturization and power consumption. The key challenge remains providing sufficient engineering control over the sensor microstructure as to ensure high performance and good reproducibility.

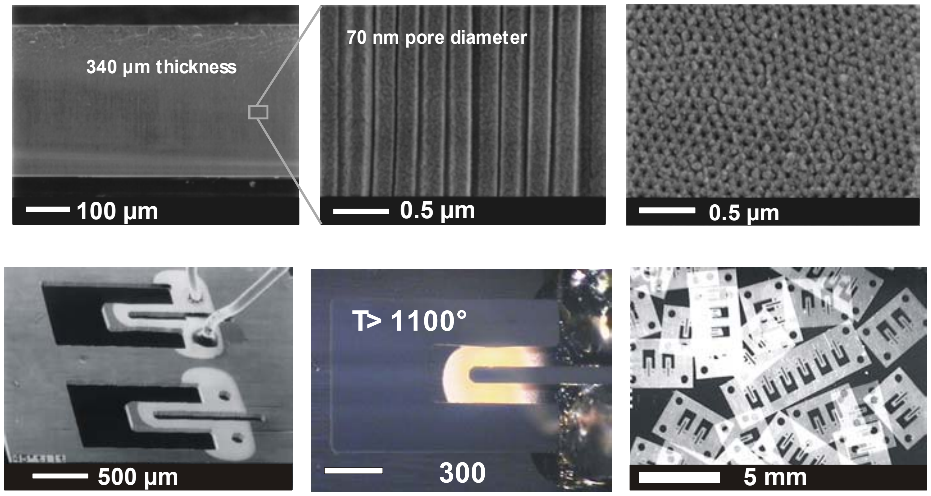

Figure 7. Microstructure of the AAO material (top) and representative sensor devices prepared from the material.

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